Available online at www.elixirpublishers.com (Elixir International Journal)

Earth Science

Elixir Earth Sci. 101 (2016) 44049-44054

Chlorophenolics Detection and Degradation in Paper Mill Wastewater

Parveen Kumar¹, Satish Kumar² and Nishi K. Bhardwaj³

¹Amity School of Earth and Environmental Sciences, Amity University Haryana, Gurgaon – 122413, Haryana, India. ²Department of Paper Technology, IIT Roorkee, Saharanpur Campus, Saharanpur – 247001, U.P., India.

³Avantha Centre of Industrial Research and Development, Paper Mill Campus, Yamuna Nagar – 135001, Haryana, India.

ARTICLE INFO

ABSTRACT

Article history: Received: 18 June 2016; Received in revised form: 10 December 2016; Accepted: 22 December 2016;

Keywords Chlorophenolics, Paper mill effluent, Photocatalysis, Titanium dioxide. The release of chlorophenolics in pulp bleaching wastewater is a threat to the aquatic ecosystems. The chlorophenolics can migrate throughout the biosphere and pose serious health hazard. The work is aimed to detect chlorophenolics using GC-MS and evaluate the effectiveness of TiO₂ photocatalysis for their degradation in the paper mill wastewaters. Four type of chlorophenolics i.e. chlorophenols (CP), chloroguaiacols (CG), chlorocatechols (CC), and chlorosyringaldehyde (CSA) are detected in the wastewaters. The wastewaters are subjected to photocatalysis with UV radiation under optimum conditions (TiO₂ = 0.50 g/L, pH = 7.0, time = 4 hr, and H₂O₂ = 15 mM/L). UV/TiO₂/H₂O₂ process has been found to be more efficient for the degradation of chlorophenolics with 68% and 75% removal of chlorophenolics for primary clarified (PC) and biotreated (BT) wastewaters, respectively, as compared to UV/TiO₂ process. The Monochlorophenols (MCP) are removed to the maximum extent followed by di- (DCP) and trichlorophenols (TCP).

Introduction

Chlorophenolics are particular class of priority pollutants listed by the US EPA under the Clean Water Act [1, 2] and the European Decision 2455/ 2001/EC [3]. Chlorophenolics are being discharged continually into the aquatic ecosystems by various anthropogenic activities, e.g. chlorine pulp bleaching, chlorination of drinking water, and incineration [4-6]. Chlorophenolics are generated as residual lignin (2.5-4%) degradation products during pulp bleaching with chlorination processes. The chromophoric and highly oxidised, polymeric lignin derivatives produced during pulp bleaching give a dark colour to the wastewater [7]. The chlorophenolics which get adsorbed on activated charcoal are collectively estimated as adsorbable organic halides (AOX) [8].

The discharge of pulp bleaching wastewaters with high AOX level into the aquatic environment is one of the major problems for the paper mills. The high molecular weight (HMW >1000 Dalton) (~80%) chlorophenolics are believed to be stable and biologically inert [9]. While, the low molecular weight (LMW <1000 Dalton) (~20%) fraction is mutagenic and toxic. LMW compounds are biorecalcitrant and biomagnify [10, 11]. Many chlorophenolics are toxic and migrate widely throughout the biosphere and eventually concentrate in the adipose tissue of organisms [12]. These pollutants pose a serious health concern owing to their genotoxicity and high endocrine disrupting potential [13]. 2,4dichlorophenol (2,4-DCP), 2,4,5-trichlorophenol (2,4,5-TCP), pentachlorophenol (PCP), chlorinated furans, and chloroform are carcinogenic, where as chlorocatechols (CC) are strongly mutagenic [14]. Thyroid dysfunction, growth retardation, decreased fertility, genotoxicity, mutagenicity, feminization or masculinization of biota are a few reported adverse health effects of chlorophenolics [15]. The chlorophenolics toxicity depends on the number and position of chlorine atoms on the benzene ring relative to the hydroxyl group [16].

© 2016 Elixir All rights reserved.

The wastewater treatment processes (physical and biological) utilized by Indian paper mills are inefficient for chlorophenolics and colour removal [17]. Hence, adoption of advanced oxidation processes (AOPs), e.g. Fe(II)/Fe(III)+H₂O₂, UV/H_2O_2 , UV/O_3 , $UV/{Fe(II)/Fe(III)+H_2O_2}$, $UV/catalyst/H_2O_2$, is needed. AOP's involve in-situ generation of hydroxyl radicals (OH') which are able to convert a wide range of pollutants into relatively harmless end products i.e. CO₂, H₂O, NO₃⁻, PO₄⁻³⁻, and halide ions [18, 19]. The TiO2 photocatalysis has demonstrated promising results for the degradation of organic producing persistent pollutants and more biodegradable and less toxic substances [20, 21].

The TiO₂ irradiation with light ($\lambda < 390$ nm), having energy $\geq 3.2 \text{eV}$ (band gap energy), produce a hole (h⁺) and electron (e) pair in the valence and conduction bands, respectively. The e^{-}/h^{+} pair can either recombine and dissipate the absorbed energy as heat or contribute in pollutants degradation reactions. The h⁺ can either directly oxidize the adsorbed pollutants or produce OH' radicals (from H₂O_{ads}/OH⁻_{ads}). OH can also oxidize pollutants nonselectively. The e is captured by adsorbed O₂ to form superoxide radical (O_{2ads}). Thus prevent e^{-}/h^{+} re-combination. The O⁻_{2ads} can further contribute in pollutant degradation reactions [22]. The H₂O₂ produce more OH radicals by absorbing light. Hence, the addition of H₂O₂ to the system improves the efficiency of the photocatalysis. The work is aimed to detect the chlorophenolics in paper mill wastewaters and evaluate efficiency of UV/TiO2 and UV/TiO2/H2O2 processes for their degradation.



44049



Experimental Materials

The primary clarified (PC) and biotreated (BT) wastewaters are received from a paper mill which uses OCE_{OP}HH (O, C, E_{OP}, and H represent O₂ delignification, elemental chlorine, O2 and H2O2 reinforced alkaline extraction, and hypochlorite stages, respectively) bleaching sequence for brightening mixed hardwood (eucalyptus and poplar) kraft pulp. TiO₂ and H₂O₂ (30%) (Fisher Scientific, SQ grade) are used as photocatalyst and oxidant, respectively. TiO₂ powder is predominantly anatase (99.97 wt%) (X-ray Diffractometer, Bruker AXS D8) with 50-150 nm particle size (FE-SEM) (Fig. 1). The BET surface area and total pore volume of TiO_2 are 26.11 m²/g and 0.0131 m³/g, respectively (N₂ adsorption, Micromeritics: Chemi Soft TPx V1.02). The chlorophenols (CP), used as reference compounds, are procured from Aldrich (Mil-waukee, USA) and Sigma (St. Louis, USA). Chlorocatechols (CC), chloroguaiacols (CG), chlorovanillins (CV), chlorosyringols (CS), and chlorosyringaldehydes (CSA) are purchased from Helix Biotech Corporation (Richmand, B.C. Canada). HPLC grade n-hexane and acetone, and LR grade diethyl ether are used as solvents. Analytical grade acetic anhydride is used after double distillation. The standard stock solutions of individual chlorophenolics are prepared in acetone/ water (10:90). The pH of the aqueous solutions and wastewaters are adjusted by 1 M NaOH or H₂SO₄ solution.

Photocatalysis

The photocatalysis experiments are performed in a UV reactor (timber-framed) fitted with 4 UV tubes each of 18 W. The 500 mL wastewater is adjusted to the desired pH, TiO₂ added, and the mixture is magnetically stirred for 30 min in the dark before UV irradiation and H₂O₂ addition, to ensure the adsorption/ desorption equilibrium. The photocatalysis experiments are carried out under optimum conditions (TiO₂ = 0.5 g/L, pH 7.0, H₂O₂ 15 mM/L, and time = 4 hr) in batch mode with complete mixing at ambient conditions [23]. The water loss is made up by adding distilled water at the end of the experiment. The catalyst separation after photocatalysis is achieved by solution pH adjustment to 7.0 and subsequent settling for 5 h. The supernatant is collected and analyzed for contaminants degradation. The experiments are performed in duplicate and average values reported.

Analytical Methods

The wastewaters are characterized for biochemical oxygen demand (BOD), chemical oxygen demand (COD), colour, pH, AOX, and chlorophenolics before and after photocatalysis. The colour is measured (465 nm) with a UV-VIS spectrophotometer (SPEKOL 2000, Analytic Jena). A pH meter (TOSHNIWAL) is used to measure the pH. BOD and COD are measured as per standard procedures [24]. The AOX is analyzed using Dextar AOX analyzer (ECS 1200, Thermo Electron Corporation) by column method. The optimum photon flux is estimated to be 2.28×10^{-6} qnp/ Einstein s⁻¹ at 15 cm from UV lamps by ferrioxalate actinometer [25].

The chlorophenolics are analyzed using Gas chromatograph (GC) – mass spectrometer (MS) (Trace GC Ultra - DSQ, Thermo Electron Corporation). The extraction of chlorophenolics from the wastewaters is carried out as per the method given by Lindstrom and Nordin [26]. The extracted samples are derivatized with acetic anhydride [27].





The readily volatile chlorophenolics acetyle derivative $(1.0 \ \mu L)$ is injected into the GC column (TR-5 capillary column: 30 m x 0.25 mm x 0.25 µm, containing 5% phenyl methyl polysiloxane) for the separation of target analytes. The GC oven temperature is held at 45 °C (1 min) and raised to 280 °C (6 °C/min). The final temperature (280 °C) is maintained for 25 min. The injector, mass transfer line, and ion source temperatures are set at 210 °C, 280 °C, and 200 °C, respectively. The helium (He) is used as carrier gas (1 mL/min). The MS is run in the electron impact ionisation (EI) mode (70 eV) with 100 µA emission current. The full scan data is acquired by scanning from 42-336 m/z (216.7 amu/sec) at fore pressure between 38-45 mTorr. The injection is performed in the splitless mode. The chlorophenolics are initially detected by matching their mass spectrum with the NIST library. Once the main peaks are identified, pure standard solutions of chlorophenolics are injected into the GC-MS for determining retention times (RT) of respective chlorophenolics and formation of calibration curve. The quantitative analysis is done using calibration curve and by extraction efficiency estimation of individual chlorophenolics. The gas chromatogram of a mixture of 26 reference chlorophenolic compounds is shown in Fig. 2. The respective retention time (RT) and mass/charge (m/z) values are depicted in Table 1.

Results and Discussion

The average analytical characteristics of PC and BT paper mill wastewaters utilized for the photocatalysis are summarized in Table 2 and 3. The six categories of chlorophenolic compounds, i.e. CP, CG, CC, CV, CS, and CSA in terms of chemical family, are identified by GC-MS in the wastewaters (Fig. 3a and 3c). The CP and CG are the main components amongst the identified chlorophenolics. Other chlorophenolics are detected in trace amounts ($\leq 1\%$). TCP are the major contributors for PC wastewater followed by DCP and MCP. While, for BT wastewater, DCP are present in the highest amount followed by TCP and MCP (Fig. 3b and 3d).



Figure 2. Chromatogram showing separation of a mixture of pure chlorophenolic compounds

Table	1.	Retention	time	(RT)	and	base	peak	(m/z)	of
chloro	phe	enolic refere	ence c	ompoi	inds				

S. No.	Name of Compound	RT (minutes)	Base Peak (m/z)		
1.	3-CP	14.20	127.9		
2.	4-CP	14.36	127.9		
3.	2,6-DCP	16.52	161.9		
4.	2,5-DCP	16.96	161.9		
5.	2,4-DCP	16.98	161.8		
6.	2,3-DCP	17.69	161.8		
7.	3,4-DCP	18.27	161.9		
8.	4-CG	18.70	157.9		
9.	2,4,5-TCP	19.07	195.8		
10.	2,3,6-TCP	20.01	195.8		
11.	2,3,5-TCP	20.17	195.9		
12.	2,4,6-TCP	20.31	195.8		
13.	4,5-DCG	21.19	191.9		
14.	2,3,4-TCP	21.23	195.8		
15.	4,6-DCG	22.27	191.9		
16.	3,6-DCC	22.50	177.9		
17.	3,5-DCC	22.77	177.9		
18.	3,4,6-TCG	23.16	225.9		
19.	3,4,5-TCG	24.40	225.8		
20.	4,5,6-TCG	25.07	225.9		
21.	5,6-DCV	25.85	219.9		
22.	PCP	26.22	265.7		
23.	2,3,5,6-TCG	26.66	261.8		
24.	TCS	26.96	255.8		
25.	Tet-CC	28.31	247.8		
26.	2,6-DCSA	28.59	249.9		

 Table 2. Average analytical characteristics of PC and BT wastewaters

S. No.	Parameter	PC	BT
1.	COD (mg/L)	1092	246
2.	BOD (mg/L)	274	29
3.	BOD/COD ratio	0.25	0.12
4.	Color (mg Pt-Co/L)	2066	1012
5.	pН	7.5	7.4
6.	AOX (mg/L)	15.8	6.6

2,3-DCP and 2,3,5-TCP are identified only in BT wastewater. This may be due to their possible dilution in the influent of primary clarifier and concentration during biological treatment. 2,5-DCP, 4,6-DCG, and 3,4,6-TCG are present in higher quantity in BT wastewater in comparison to PC wastewater. This may be caused by the possible transformation of one compound into another during biological treatment or concentration because of treatment system residence time [28].

The biological treatment is able to meet wastewater discharge standards for BOD (30 mg/L) and COD (350 mg/L) in case of large pulp and paper news print/ rayon grade plants [29]. But, the chlorophenolics and colour persist because of low efficiency of biological processes for their degradation. The BOD/COD ratio of the wastewaters is low (0.25 for PC wastewater and 0.12 for BT wastewater) indicating low biodegradability of the organics. Therefore, the photocatalytic treatment of PC and BT paper mill wastewaters have been investigated with UV/TiO2 and UV/TiO2/H2O2 processes for the degradation of chlorophenolics. The initial COD of the wastewater should be lower than 800 mg/L for the successful catalysis. The excess organic matter tends to recover the catalyst surface by adsorption and causes scattering of radiation [30]. Therefore, PC wastewater is diluted to 500 mg/L of COD before photocatalysis while BT wastewater is used in original.

Table 3. Chlorophenolics removal (%) for PC and BT wastewaters with UV/TiO₂ and UV/TiO₂/H₂O₂ processes

S. No.	Name of	Ci± SI)	Removal (%)			
	Compound	(µg/L)		UV/TiO ₂		UV/TiO ₂ /H ₂ O ₂	
		PC*	BT	PC	BT	РС	BT
1.	3-CP	2.20	1.70	65	75	73	78
2.	4-CP	0.90	0.90	74	86	86	91
3.	2,6-DCP	1.10	1.69	53	64	59	85
4.	2,5-DCP	0.54	1.12	76	76	ND	79
5.	2,4-DCP	1.46	1.74	56	68	64	71
6.	2,3-DCP	ND	0.05	ND	80	ND	ND
7.	3,4-DCP	0.59	0.94	75	75	86	78
8.	4-CG	0.56	1.01	68	69	74	76
9.	2,4,5-TCP	4.87	3.74	48	58	53	65
10	2,3,6-TCP	0.06	ND	64		91	
11.	2,3,5-TCP	ND	0.04		ND		ND
12.	2,4,6-TCP	0.51	0.07	57	71	70	ND
13.	4,5-DCG	0.97	1.41	67	65	82	68
14.	2,3,4-TCP	0.09	0.15	67	60	ND	87
15.	4,6-DCG	0.46	1.73	69	74	88	76
16.	3,6-DCC	0.11	ND	72		81	
17.	3,4,6-TCG	0.40	1.18	51	67	66	75
18.	4,5,6-TCG	0.02	ND	ND		ND	
19.	5,6-DCV	0.06	ND	82		ND	
20.	TCS	0.03	0.01	ND	ND	ND	ND
21.	2,6-DCSA	0.16	0.08	71	ND	84	ND
Total		15.09	17.56	59	68	68	75

ND – not detected; Ci: Initial concentration; *Concentration after dilution to 500 mg/L COD.





(a)

(c)



Figure 3. Proportion (%) of chlorophenolics by chemical family and number of attached chlorine atoms for PC (a-b) and BT (c-d) wastewaters

PC Wastewater Treatment

CV and CS with UV/TiO₂/H₂O₂ process and CS with UV/TiO₂ process are degraded below detection. The UV/TiO₂/H₂O₂ process degraded remaining chlorophenolics in the order: CSA >CC >CG >CP (Fig. 4a).



Figure 4. Removal (%) of chlorophenolics by chemical family (a) and number of attached chlorine atoms (b) for PC wastewater



Figure 5. Removal (%) of chlorophenolics by chemical family (a) and number of attached chlorine atoms (b) for BT wastewater

While, UV/TiO₂ process degraded chlorophenolics in the order: CV >CC >CSA >CG >CP (Fig. 4a). 2,3,6-TCP is degraded to the maximum extent followed by 4-CP and 3,4-DCP >3-CP >2,4,6-TCP by treatment with UV/TiO₂/H₂O₂ process. The remaining CP's are degraded between 53-66%. While, UV/TiO₂ process degraded 2,5-DCP to the maximum

extent followed by 3,4-DCP >4-CP >2,3,4-TCP. The remaining CP's are degraded in the range of 48-65%. UV/TiO₂/H₂O₂ process degraded CGs in the order 4,6-DCG >4,5-DCG >4-CG >3,4,6-TCG. 2,6-DCSA and 3,6-DCC are removed up to 84 and 81%, respectively. While, UV/TiO₂ process degraded CGs in the order 4,6-DCG >4-CG >4,5-DCG >3,4,6-TCG. 5,6-DCV is degraded up to 82% followed by 3,6-DCC (72%) and 2,6-DCSA (71%) by treatment with UV/TiO₂ process. 2,5-DCP, 2,3,4-TCP, 4,5,6-TCG, 5,6-DCV, and TCS with UV/TiO₂/H₂O₂ process and 4,5,6-TCG and TCS with UV/TiO₂ process are degraded below detection (Table 3). The chlorophenolics degradation followed the order: 4-CP >3-CP, 2,5-DCP >3,4-DCP >2,4-DCP >2,6-DCP with UV/TiO₂ process and $UV/TiO_2/H_2O_2$ process degraded the same in the order: 2,3,4-TCP >2,3,6-TCP >2,4,6-TCP >2,4,5-TCP. The similar orders of degradation of chlorophenolics have been reported in the literature [31].

BT Wastewater Treatment

While in case of BT wastewater, CS and CSA are degraded below detection after treatment with both the processes. The higher degradation of CP and CG is achieved with UV/TiO₂/H₂O₂ process as compared to UV/TiO₂ process (Fig. 5a). 4-CP is degraded up to the maximum extent followed by 2,3,4-TCP >2,6-DCP >2,5-DCP after treatment with $UV/TiO_2/H_2O_2$ process. The remaining CP's are degraded in the range of 65-78%. While, UV/TiO₂ process degraded CPs in the order: 4-CP >2,3-DCP >2,5-DCP >3-CP = 3,4-DCP. The remaining CP's are degraded in the range of 58-71%. Among CG, UV/TiO₂/H₂O₂ process degraded CG's in the order: 4-CG = 4,6-DCG >3,4,6-TCG >4,5-DCG (68%). While, UV/TiO₂ process degraded CG's in the order: 4,6-DCG >4-CG >3,4,6-TCG >4,5-DCG. 2,3-DCP, 2,3,5-TCP, 2,4,6-TCP, TCS, 2,6-DCSA and 2,3,5-TCP, TCS, 2,6-DCSA are degraded below detection after treatment with UV/TiO₂/H₂O₂ and UV/TiO₂ processes, respectively (Table 3).

MCP's are degraded to the maximum extent followed by DCP and TCP from PC and BT wastewaters after treatment with both the processes (Fig. 4b and 5b). The photocatalytic degradation of aromatics depends on the substituent group and MCP's degrade faster than DCP's or TCP's [31]. The rate of degradation decreases as the number of Cl atoms on the phenolic ring increase. The sites on the aromatic ring, which are not occupied by Cl atoms, are usually attackd by OH' radicals. Therefore, higher number of Cl atoms on the aromatic ring decreases the reactivity towards the OH' radicals [32, 33]. Cl, due to its e withdrawing nature, decreases the e density of aromatic ring and chlorophenolics reaction ability as the Cl content increases [34]. The higher chlorophenolics degradation is achieved with UV/TiO₂/H₂O₂ process (PC wastewater: 68% and BT wastewater: 75%) as compared with UV/TiO₂ (PC wastewater: 59% and BT wastewater: 68%) process (Table 3). H_2O_2 can accept conduction band e⁻ thus prevent e⁻/h⁺ recombination and can additionally produce OH' radicals easily by splitting as compared to H₂O. The H₂O₂ addition has been reported to increase rate of reaction by 20-30% [35, 36].

The higher chlorophenolics degradation is observed for the BT wastewater as compared to the PC wastewater. The biological treatment may convert some functional groups of organic contaminants to easily oxidisable form which are then easily degraded during photocatalysis [37]. This may also be caused by the initial low organic load of the BT wastewater as compared to the PC wastewater. The BOD/COD ratio improved to 0.34 and 0.31 for PC wastewater and 0.22 and 0.21 for BT wastewater after photocatalysis with UV/TiO₂/H₂O₂ and UV/TiO₂ processes, respectively [38]. These findings indicate degradation of chloroorganics and toxicity decrease.

Yeber et al. [39] stated that photocatalysis could be an excellent pre-oxidation step to the biological treatment as the biodegradability of the residual organic matter is improved during photocatalysis. The partial mineralisation and structural changes in the organic contaminants are the basis for BOD/COD ratio improvement, chlorinated phenols and reduction toxicity of the wastewaters [40]. The chlorophenolics in paper mill wastewaters are degraded to different extent after photocatalysis. This may be because of the initial contaminant load, differential adsorption over catalyst surface, number and position of Cl atoms on the aromatic ring and reaction intermediates which compete for photoactive sites [41].

Conclusion

Based on the present work, the following conclusions are drawn:

1. The major compounds identified in PC and BT wastewaters are DCPs and TCPs which impart high toxicity to paper mill wastewaters.

2. The UV/TiO₂/H₂O₂ process is found to be more effective for the degradation of chlorophenolics from the paper mill wastewaters.

3. The photocatalysis improved biodegradability of the wastewaters by degradation of toxic compounds. Hence, the photocatalysis as a pre-treatment step to biological treatment is a good option to improve the biodegradability of the pollutants for their further degradation by the biological processes.

Acknowledgement

The research grant provided by Ministry of Human Resource Development, Government of India, the facilities utilised, and support received at Department of Paper Technology, IIT Roorkee is gratefully acknowledged.

References

[1] EPA, 2002. http://www.scorecard.org.

[2] L. H. Keith and W. A. Telliard, "Priority polluants - a perspective view," Environ. Sci. Technol., vol. 13 (4), pp. 416-423, 1979.

[3] The European Parliament and of the Council, "EC Decision 2455/2001/EC of the European Parliament and of the Council of 20 November 2001: Establishing the List of Priority Substances in the Field of Water Policy and Amending Directive 2000/60/EC," The European Parlia-ment and of the Council, 2001.

[4] S. K. Kansal, M. Singh, and D. Sud, "Optimization of photocatalytic process parameters for the degradation of 2,4,6-trichlorophenol in aqueous solutions," Chem. Eng. Commun., vol. 194 (6), pp. 787-802, 2007.

[5] T. Pandiyan, O. M. Rivas, J. O. Martinez, G. B. Amezcua, and M. A. M. Carrillo, "Comparison of methods for the photochemical degradation of chlorophenols," J. Photoch. Photobio. A, vol. 146 (3), pp. 149-155, 2002.

[6] C. Sharma, S. Mohanty, S. Kumar, and N. J. Rao, "Gas chromatographic analysis of chlorophenolic, resin and fatty acids in effluents from bleaching processes of agricultural residues," Int. J. of Environ. An. Ch., vol. 64 (4), pp. 289-300, 1996.

[7] D. Livernoche, L. Jurasek, M. Desrochers, J. Dorica, and I. A. Veliky, "Removal of color from kraft mill wastewater with cultures of white rot fungi and with immobilized mycelium of coriolus versicolor," Biotechnol. Bioeng., vol. 25, pp. 2055-2065, 1983.

[8] C. W. Dence and D. W. Reeve, "Pulp Bleaching -Principles and Practice," TAPPI Press, Atlanta, Georgia, pp. 752, 1996.

[9] J. K. Jokela and M. Salkinoja-Salonen, "Molecular weight distributions of organic halogens in bleached kraft pulp mill effluents," Environ. Sci. Technol., vol. 26, pp. 1190-1197, 1992.

[10] P. Ander, K. E. Eriksson, M. C. Kolar, K. Kringstad, U. Rannung, and C. Ramel, "Studies on the mutagenic properties of bleaching effluents (on Escherichia coli and Salmonella typhimurium)," Sven. Papperstidn., vol. 80, pp. 454-459, 1977. [11] R. M. B. O. Duarte, E. B. H. Santos, and A. C. Duarte, "Spectroscopic characteristics of ultrafiltration fraction of fulvic and humic acids isolated from a eucalyptus bleached kraft pulp mill effluent," Water Res., vol. 37 (17), pp. 4073-4080, 2003.

[12] L. R. Sunito, W. Y. Shiu, and D. Mackay, "A review of the nature and properties of chemicals present in pulp mill effluents," Chemosphere, vol. 17, pp. 1249-1290, 1988.

[13] S. K. Kansal and M. Chopra, "Photocatalytic degradation of 2,6-dichlorophenol in aqueous phase using titania as a photocatalyst," Engineering London, vol. 4, pp. 416-420, 2012.

[14] D. V. Sawant and R. Ranade, "Biodegradation of AOX from paper and pulp industry wastewater," Interaction Meet on Environmental Impact of Toxic Substances Released in Pulp and Paper Industry, pp. 41-43, 2002.

[15] K. R. Munkittrick, M. E. McMaster, L. H. McCarthy, M. R. Servos, and G. J. Van Der Kraak, "An overview of recent studies on the potential of pulp mill effluents to impact reproductive function in fish", Jpn. J. Tox. Env. Health, vol. 1, pp. 101-125, 1998.

[16] R. Orrego, J. Guchardi, L. Beyger, R. Krause, and D. Holdway, "Comparative embryo toxicity of pulp mill extracts in rainbow trout (Oncorhynchus mykiss), American flagfish (Jordanella floridae) and Japanese medaka (Oryzias latipes)," Aquat. Toxicol., vol. 104, pp. 299–307, 2011.

[17] K. Lindstrom and M. Mohamed, "Selective removal of chlorinated organics from kraft mill total effluents in aerated lagoons," Nord. Pulp Pap. Res. J., vol. 3 (1), pp. 26-33, 1988.

[18] Y. Ku and C. B. Hsieh, "Photocatalytic decomposition of 2,4-dichlorophenol in aqueous TiO₂ suspensions," Water Res., vol. 26 (11), pp. 1451-1456, 1992.

[19] O. Carp, C. L. Huisman, and A. Reller, "Photoinduced reactivity of titanium dioxide," Prog. Solid State Ch., vol. 32, pp. 33-177, 2004.

[20] M. N. Chong, B. Jin, C. W. K. Chow, and C. Saint, "Recent developments in photocatalytic water treatment technology: a review," Water Res., vol. 44, pp. 2997- 3027, 2010.

[21] S. Mishra, V. Meda, A. K. Dalai, D. W. McMartin, J. V. Headley, and K. M. Peru, "Photocatalysis of naphthenic acids in water," J. Wat. Res. Prot., vol. 2 (7), pp. 644-650, 2010.

[22] R. Thiruvenkatachari, S. Vigneswaran, and I. S. Moon, "A review on UV/TiO_2 photocatalytic oxidation process," Korean J. Chem. Eng., vol. 25 (1), pp. 64-72, 2008.

[23] P. Kumar, S. Kumar, N. K. Bhardwaj, and A. K. Choudhary, "Optimization of process parameters for the photocatalytic treatment of paper mill wastewater," Environ. Eng. Manag. J., vol. 10 (5), pp. 595-601, 2011.

[24] L. S. Clesceri, A. E. Greenberg, and A. D. Eaton, "Standard methods for the examination of water and wastewater," 20th ed. Pub. American Public Health Association, pp. 2 (3), 4 (87), 5 (3), and 5 (15), 1998. [25] H. J. Kuhn, S. E. Braslavsky, and R. Schmidt, "Chemical Actinometry, IUPAC Technical Report," Pure Appl. Chem., vol. 76, pp. 2105-2146, 2004.

[26] K. Lindstrom and J. Nordin, "Gas chromatography mass spectrometry of chlorophenols in spent bleach liquors," J. Chromatogr., vol. 128, pp. 13-26, 1976.

[27] K. Abrahamsson and T. M. Xie, "Direct determination of trace amounts of chlorophenols in fresh water, wastewater and sea water," J. Chromatogr., vol. 279, pp. 199-208, 1983.

[28] D. B. Spengel, B. Bicknell, D. F. Anderson, M. Smith, and D. G. Bodien, "A comparison of chlorinated phenolic compound concentrations and loadings in bleach-plant and treatment-system samples at eight mills," TAPPI J., vol. 77 (11), pp. 155-166, 1994.

[29] The Environment (Protection) Rules, Large pulp & paper news print/ rayon grade plants of [capacity above 24000 MT per annum], 1986, http://cpcb.nic.in/Industry-Specific-Standards/Effluent/445.pdf.

[30] P. R. Gogate and A. B. Pandit, "A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions," Adv. Environ. Res., vol. 8, pp. 501-551, 2004.

[31] C. P. Huang, C. Dong, and Z. Tang, "Advanced chemical oxidation: its present role and potential future in hazardous waste treatment," Waste Manage., vol. 13, pp. 361-377, 1993.

[32] J. F. Benitez, J. B. Heredia, J. L. Acero, and F. J. Rubio, "Contribution of free radicals to chlorophenols decomposition by several advanced oxidation processes," Chemosphere, vol. 41, pp. 1271–1277, 2000.

[33] H. Ilyas, I. A. Qazi, W. Asgar, M. A. Awan, and Z. U. D. Khan, "Photocatalytic degradation of nitro and chlorophenols using doped and undoped titanium dioxide nanoparticles," J. Nanomater., vol. 2011, pp. 1-8, 2011.

[34] P. Saritha, D. Samuel Suman Raj, C. Aparna, P. Nalini Vijaya Laxmi, V. Himabindu, and Y. Anjaneyulu, Degradative oxidation of 2,4,6 trichlorophenol using advanced oxidation

processes – a comparative study, Water Air Soil Poll., vol. 200, pp. 169–179, 2009.

[35] C. Sattler, L. de Oliveira, M. Tzschirner, A. E. H. Machado, Solar photocatalytic water detoxification of paper mill effluents, Energy, vol. 29, pp. 835-843, 2004.

[36] A. E. H. Machado, J. A. de Miranda, R. F. de Freitas, E. T. F. M. Duarte, L. F. Ferreira, Y. D. T. Albuquerque, R. Ruggiero, C. Sattler, and L. de Oliveira, Destruction of the organic matter present in effluent from a cellulose and paper industry using photocatalysis, J. Photoch. Photobio. A, vol. 155, pp. 231-241, 2003.

[37] I. A. Balcioglu and I. Arslan, Application of photocatalytic oxidation treatment to pretreated and raw effluents from the kraft bleaching process and textile industry, Environ. Pollut., vol. 103, pp. 261-268, 1998.

[38] P. Kumar, S. Kumar, N. K. Bhardwaj, and A. K. Choudhary, Advanced oxidation of pulp and paper industry effluent, Proceedings of 2011 International Conference on Environmental and Agriculture Engineering, Chengdu, China, IPCBEE, IACSIT Press, Singapore, vol. 15, pp. 170-175, 2011.

[39] M. C. Yeber, J. Rodriguez, J. Baeza, J. Freer, C. Zaror, N. Duran, and H. D. Mansilla, Toxicity abatement and biodegradability enhancement of pulp mill bleaching effluent by advanced chemical oxidation, Water Sci. Technol., vol. 40, pp. 337-342, 1999.

[40] M. C. Yeber, J. Freer, M. Martonez, and H. D. Mansilla, Bacterial response to photocatalytic degradation of 6-chlorovanillin, Chemosphere, vol. 41, pp. 1257-1261, 2000.

[41] K. M. Parida and S. Parija, Photocatalytic degradation of phenol under solar radiation using microwave irradiation zinc oxide, Sol. Energy, vol. 80, pp. 1048-1054, (2006).